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Reliability Assessment of No-clean and Water-soluble Solder Pastes Part II

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Abstract
Looking back twenty-five years ago, the solder pastes residues had to be cleaned after reflow due to their corrosive nature: two ways of cleaning were possible, either with solvent or by using water, with or without detergent. Now the assembly world is mainly no-clean: paste formulation is safer in terms of chemical reliability and process costs are reduced without cleaning. However, some applications, i.e. military, aerospace, high frequency, semiconductor require a perfect elimination of the residue after reflow. There are several options to achieve this result: the use of a no-clean paste which residue can be removed with the most suitable cleaning method or the use of a paste designed to be cleaned, as a water-soluble solder paste.
The water-soluble solder pastes generally show great wettability because of their strong activation but they are also known to have shorter stencil life and to be more sensitive to working conditions as temperature and humidity, compared to the no-clean pastes. Additionally, with the components stand-off getting smaller and smaller, washing residues with water only is more and more challenging due to its high surface tension: the addition of detergent becomes often necessary.
The purpose of this paper is to highlight the differences between these two families of solder pastes to guide users in their choice. This will be achieved through the comparison of several recent water-soluble and no-clean formulations as far as reliability is concerned. First the printing quality will be evaluated (viscosity, tack, cold slump, printing speed according to pressure, stencil life, idle time, printing consistency). Then the reflow properties will be compared (hot slump, solderballing, reflow process window, wetting ability on different finishes). Finally the residue cleanability will be assessed. The IPC SIR will be also done to conclude the study. Both standardized tests and production tests will be used to evaluate the performance of these two kinds of solder pastes.

Introduction
Six lead-free pastes were extensively studied, three being water-soluble and three being no-clean. The first part of the study [1] focused on printing performance. The pastes were characterized using standardized tests and internally developed tests: dynamic viscosity, tackiness, slump and solderballing. The influence of accelerated storage at elevated temperature, the influence of time and conditions between printing and reflow and the influence of continuous shear according to time were shown. The printing performances were also evaluated in a printer. Although the number of pastes studied was restricted, the water-soluble pastes generally yielded results below the no-clean pastes with more sensitivity to temperature and humidity, tendency to slump during preheat and narrower printing window. Water-soluble solder pastes must be stored, handled and used with more caution before reflow.
In the second part of the paper, the reflow properties will be compared: wettability, reflow process window, anti-graping properties. Finally the residue cleanability with water, then with water and detergents will be examined. The cleanliness will be assessed using visual inspection, ionic contamination and surface insulation resistance tests.

Experiments
The pastes used for this evaluation were all made of SnAg3Cu0.5 (SAC305) alloy with type 3 (25/45 microns, -325/+500 mesh) particle size. The selected water-soluble pastes are named A, B and C and the no-clean pastes are named D, E and F. Metal content and flux designation according to J-STD-004A are given for each solder paste. A summary is done in the Table 1.

Table 1. Solder pastes characteristics

Paste	**A**	**B**	**C**	**D**	**E**	**F**
Nature	Water-soluble	Water-soluble	Water-soluble	No-clean	No-clean	No-clean
Alloy	SnAg3Cu0.5					
Particle size	Type 3					
Flux type	ORH0	ORH1	ORH1	ROL0	ROL0	ROL1
Metal Content	88.0	89.0	89.5	88.0	88.5	88.5

The wetting properties of the pastes were assessed using on cleaned copper coupons, on copper finish FR4 substrates, on test boards with several finishes, on hotplate and reflow oven. The details are described below.

Wettability on copper coupon using hotplate and reflow oven
First, a wetting test on 0.4mm thickness cleaned copper coupons was performed: the pastes were printed on substrates through a 0.250mm thick stencil with two round openings of 5mm diameter, with a distance between centers of 25mm. A set of cleaned coupons was placed on a hotplate at 250°C for immediate reflow while the other sets were submitted to

preheat before reflow, respectively during 2 minutes at 160°C and 5 minutes at 160°C. The profiles recorded on the hotplate are given below (Figure 1).

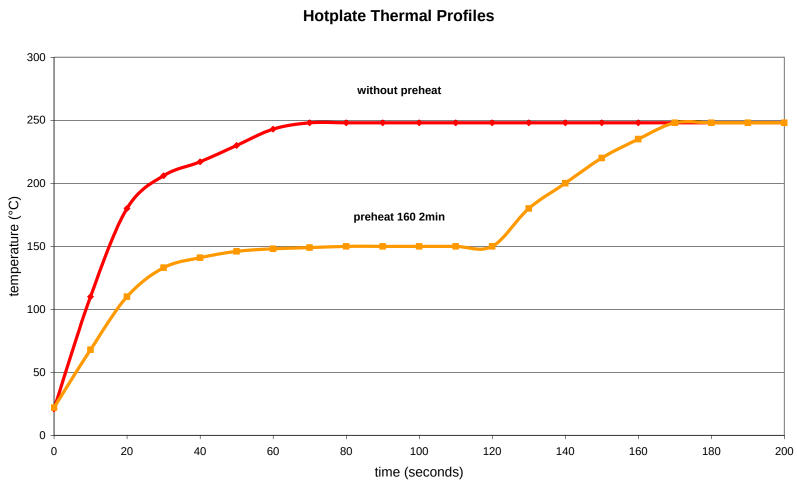


Figure 1. Hotplate thermal profiles

Second, a wetting test on the same copper coupons was done in a reflow oven (BTU VIP70 5 zones) using two profiles: P1 is a gentle profile with a short and linear preheat; P5 is a harsh profile with a long soak at high temperature. A graph of these profiles and their characteristics are given below (Figure 2 / Table 2).

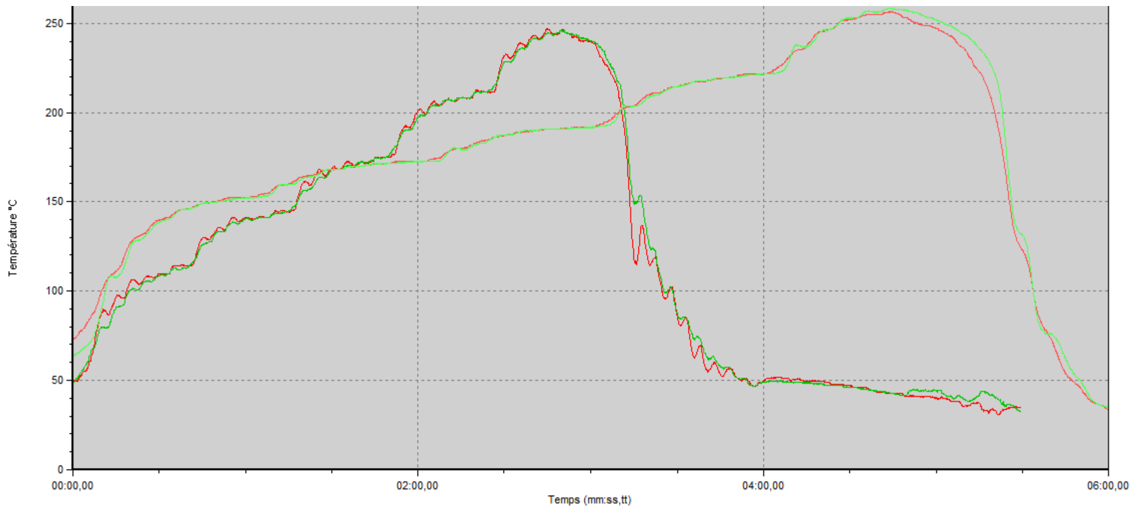


Figure 2. Thermal profiles P1 and P5

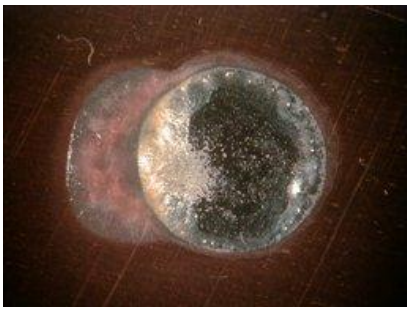
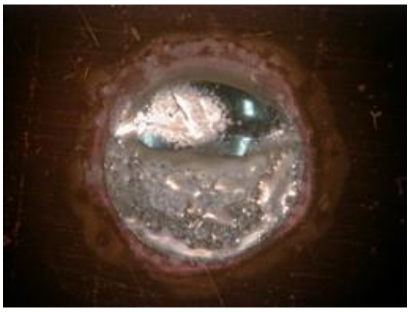
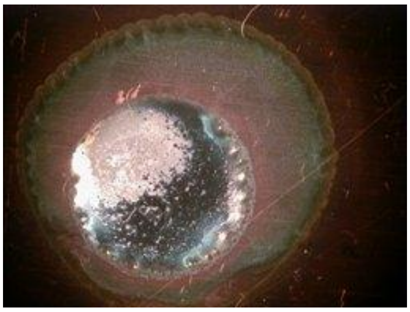
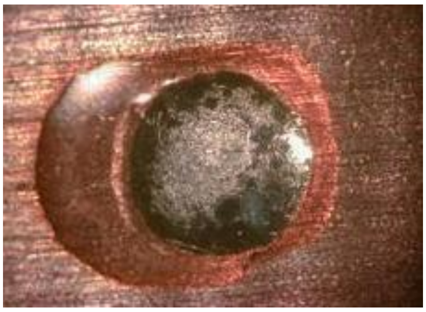
Table 2. P1 and P5 characteristics

	reflow profile P1 (short / linear preheat)		**reflow profile P5 (long / high soak)**	
	Time (s)	**Ramp rate (°C/s)**	**Time (s)**	**Ramp rate (°C/s)**
Preheat 1 (50-100°C)	25	2.0	10	5.0
Preheat 2 (100-150°C)	52	1.0	40	1.25
Preheat 3 (150-200°C)	58	0.9	139	0.36
Reflow (200°C to peak)	57	0.8	94	0.6
Total time to peak	192s		283s	
Time above 217°C (TAL)	40s		100s	
Peak temperature	248°C		257°C	
Oven temperature set-up (°C)	120/160/180/220/260		150/170/190/220/260	
Oven speed set-up	60cm/mn		35cm/mn	

After reflow, each coupon was rated according to the following criteria:
- Class 1 (C1) - Solder spreads more than printed area with no evidence of dewetting or non wetting,
- Class 2 (C2) - Solder spreads equal to printed area with no evidence of dewetting or non wetting,
- Class 3 (C3) - Solder spreads less than printed area or evidence of dewetting or non wetting.

The results are summarized in Table 3 with a few pictures.

Table 3. Wetting on copper coupons summary

Paste	A	B	C	D	E	F
Hotplate No preheat	C1	C1	C1	C2	C1	C1
Hotplate 160°C 2 min	C1	C1	C3	C2	C2	C1
Hotplate 160°C 5 min	C3	C2	C3	C3	C2	C2
Oven Short/linear profile P1	C2	C1	C2	C2	C2	C2
Oven Long/high soak P5	C3	C3	C2	C3	C2	C2
	 A-hotplate-160°C 2mn-Class 1			 A-hotplate-160°C 5mn-Class 3		
	 D-hotplate-160°C 2mn-Class 2			 E-oven-Profile P1-Class 2		

<u>Wettability on FR4 copper substrates using reflow oven</u>

The purpose was first to quantify the wetting performance of solder pastes and secondly to evaluate their ability to avoid graping. Graping phenomenon is characterized by unreflowed solder powder on the surface of solder joints. Graping is due to the consumption of the flux activators during preheating. This phenomenon is enhanced for small deposits because of the higher exposed surface area compared to the paste volume, for paste with less activation and for thermal profiles with long and high soak. To perform such tests, FR4 substrates of 1.6mm thickness with round copper pads of 5mm were used. After cleaning the substrates, the pastes were printed through a 120 microns stencil with 5 openings of respectively 5mm, 3mm, 1mm, 0.76mm and 0.38mm diameter. The substrates were placed in the reflow oven using P1 and P5 thermal profiles. Each test was done three times to assure repeatability. The diameter after reflow was measured for every pad and any sign of graping was recorded. A general view of the wetting substrate after reflow is shown in Figure 3. Examples of appearance after reflow are given in Figure 4: graping for 0.38mm diameter deposit; no graping for 0.76mm diameter deposit with the same solder paste; diameter measurement for an initial deposit of 0.38mm. Table 4 presents the mean of the measured diameters where Di states for the initial diameter after printing (mm) and Df is the diameter after reflow; The wetting percentage (Df/Di)according to paste type and thermal profile is reported as a histogram in Figure 5. Graping was only observed for pastes C and D with an initial diameter of 0.38mm.

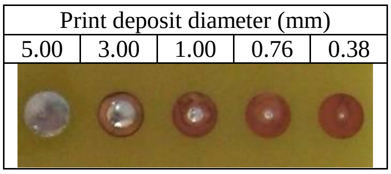


Figure 3. Wetting substrate description

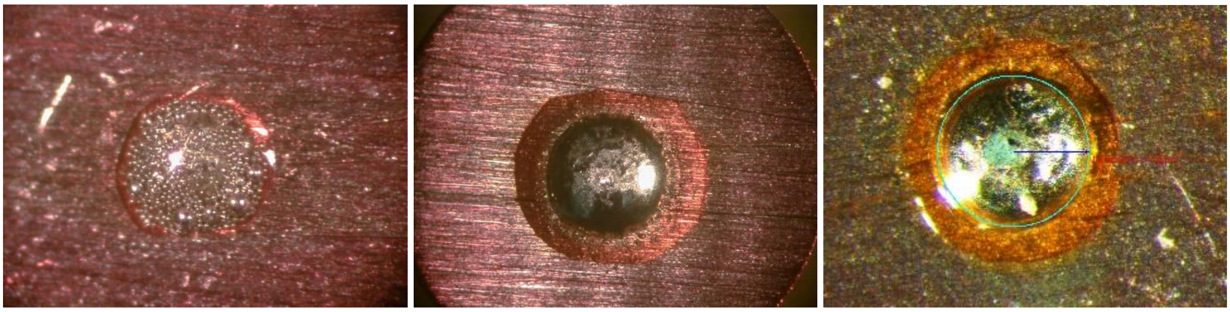


Figure 4. a) Graping on 0.38mm, b) No graping on 0.76mm, c) Diameter 0.41mm (initial 0.38mm)

Table 4. Wetting diameter

		A	B	C	D	E	F
P1	**Di (mm)**	**Df (mm)**	**Df (mm)**	**Df (mm)**	**Df (mm)**	**Df (mm)**	**Df (mm)**
	5,00	5,00	5,00	5,00	5,00	5,00	5,00
	3,00	3,20	3,25	2,96	3,00	2,98	3,20
	1,50	1,70	1,78	1,49	1,50	1,40	1,60
	0,76	0,92	0,92	0,90	0,75	0,78	0,81
	0,38	0,42	0,44	0,44	0,39	0,42	0,42
P5	**Di (mm)**	**Df (mm)**	**Df (mm)**	**Df (mm)**	**Df (mm)**	**Df (mm)**	**Df (mm)**
	5,00	5,00	5,00	5,00	5,00	5,00	5,00
	3,00	3,25	2,95	3,03	3,00	2,97	3,20
	1,50	1,75	1,50	1,58	1,50	1,44	1,58
	0,76	0,98	0,87	0,87	0,71	0,75	0,82
	0,38	0,42	0,43	0,46	0,35	0,41	0,44

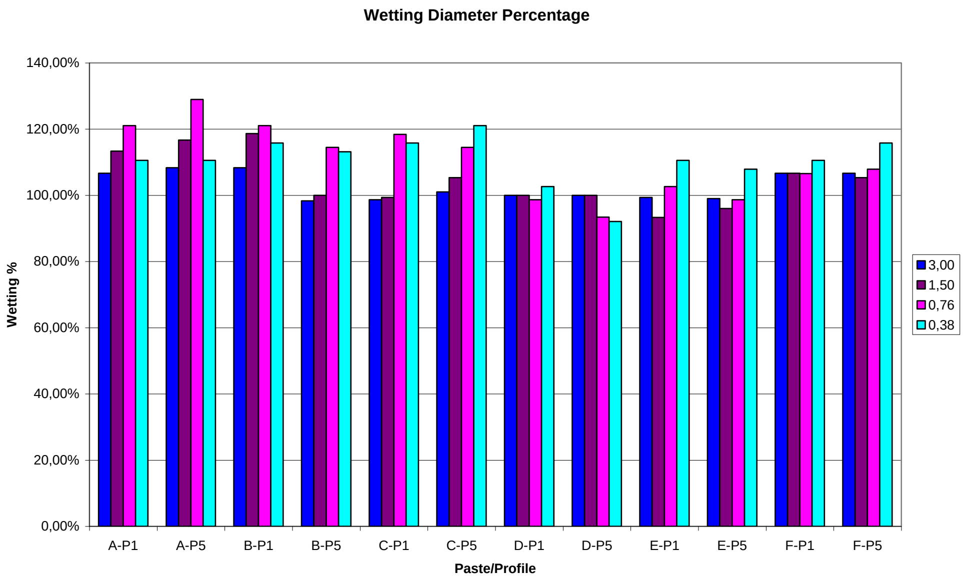
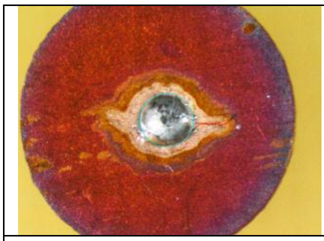
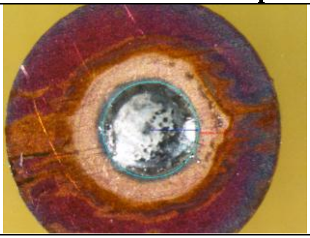
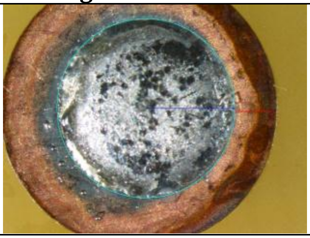
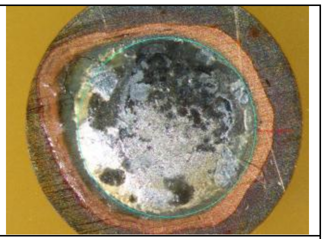
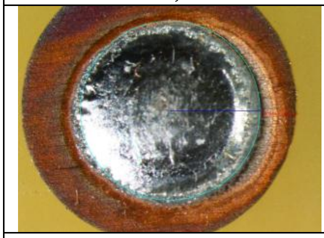
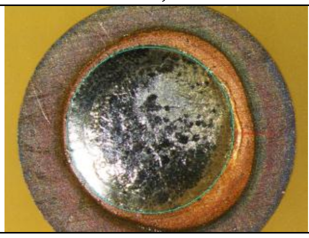
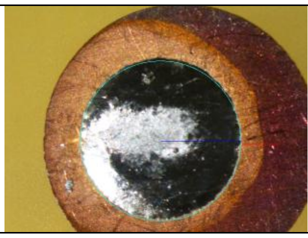
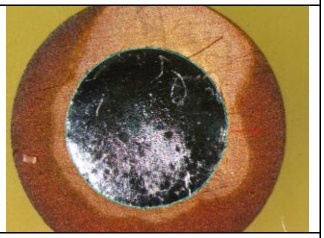


Figure 5. Graph of wetting percentage according to paste type and thermal profile

Some pictures of wetting are shown in the table below (Table 5). A, B and C solder pastes perform better than no-clean solder pastes D, E and F. Paste A has the largest wettability and paste D the lowest one. The thermal profile has no noticeable influence. The influence of the size of the initial paste deposit is relatively low for pastes D, E and F, a bit more significant for A, B and C. The wettability according the initial diameter size is different for each paste.

Table 5. Examples of wetting diameters

			
Paste A-P1-Di 0,38 / Df 0.42	Paste A-P1-Di 0,76 / Df 0.92	Paste A-P1-Di 1.50 / Df 1.70	Paste A-P5-Di 3.00 / Df 3.20
			
Paste B-P5-Di 3.00 / Df 2.95	Paste C-P5-Di 3.00 / Df 3,03	Paste D-P5-Di 3.00 / Df 3.00	Paste E-P5-Di 3.00 / Df 2.97

Wettability on test board using reflow oven

The pastes were printed through a 100µm stencil on a test board designed for wettability (Figure 6). In order to pre-oxidize the test boards, they were submitted to one prior reflow. P5 was used. Organic solderability preservative (OSP) and electroless nickel immersion gold (Enig) finishes were tested. Wetting performances were checked. Pictures of wetting on patterns A and G are given in Table 6 and Figure 7.

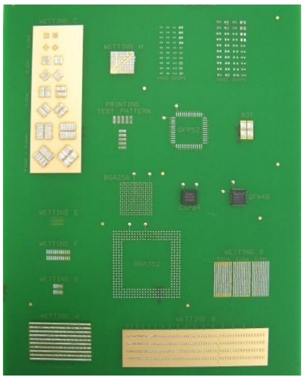
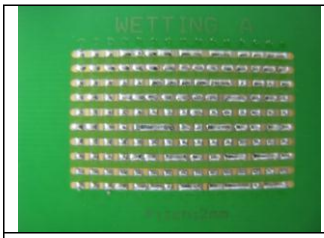
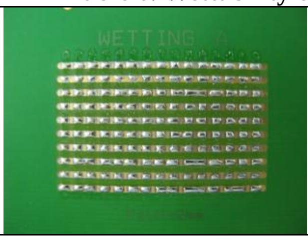
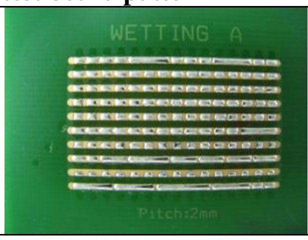
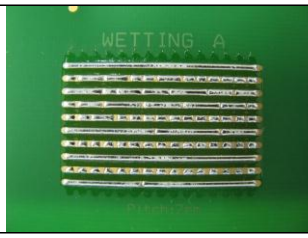
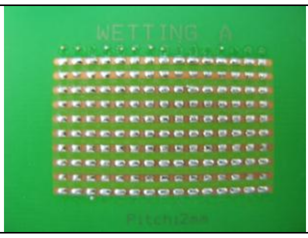
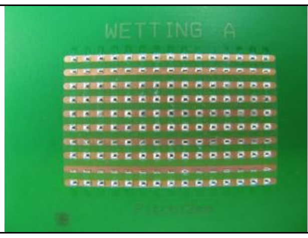
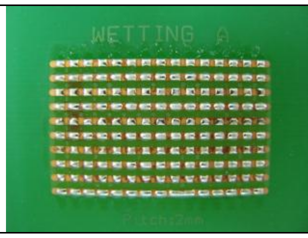


Figure 6. Wetting test board

Table 6. Wettability on test board pattern A

			
Paste A-ENIG	Paste B-ENIG	Paste E-ENIG	Paste F-ENIG
			
Paste A-OSP	Paste B-OSP	Paste D-OSP	Paste F-OSP

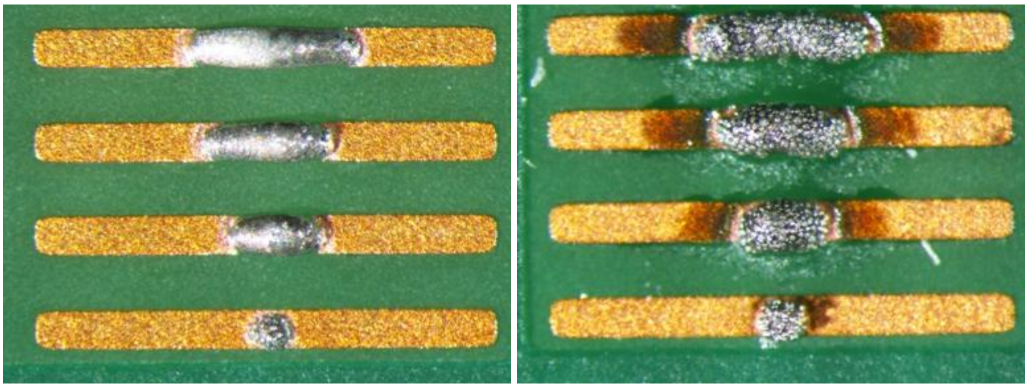


Figure 7. Wettability on test board pattern G (ENIG) a) Paste A, b) Paste D

On OSP finish, the ranking was similar to the test previously made on the FR4 copper substrate whereas the ranking on ENIG finish was dependent on paste and on pattern type. The average results are, in decreasing order of wettability: A, E and F almost equal, then C, B and D. Only the wetting properties of D were constant and always the worst.

Tombstoning

The water-soluble solder pastes being usually more prone to create tombstoning defects due to their high activation, a test was performed: forty 0603 capacitors were placed with an offset on the wetting test board comprising several aperture designs. Special reflow conditions were used, in order to observe a significant tombstoning percentage. The conditions will not be described in this paper. The experiment was repeated three times for each paste. The table below (Table 7) indicates the percentage of tombstoning observed.

Table 7. Tomsbtoning percentage

Paste	A	B	C	D	E	F
Tombstoning	13%	8%	15%	5%	4%	2%

Copper mirror

The induced corrosion on copper mirror was done according to IPC-TM-650 method 2.3.32. The evaluation was made according to J-STD-004 criteria:

- Type L - No complete breakthrough, as evidenced by white background showing through anywhere on the test spots; this condition includes discoloration of the copper due to a superficial reaction or a reduction of the thickness of the copper film without complete breakthrough,
- Type M - Partial or complete copper mirror removal in less than 50 % of test area,
- Type H - Complete copper mirror removal allowed in more than 50 % of test area.

The results were in accordance with the initial specifications of the pastes; a summary is done in the Table 8 below.

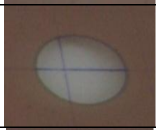
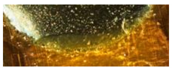
Corrosion test

The corrosion test was done according to IPC-TM-650 method 2.6.15 and the results were assessed according to J-STD-004 criteria:

- No Evidence of Corrosion - No evidence of corrosion is present,
- Minor Corrosion - Any initial change of color, which may develop when the test panel is heated during soldering, is disregarded. Discreet white or colored spots in the flux residues or a color change to greenblue without pitting of the copper or formation of excrescences is regarded as minor corrosion.
- Major Corrosion - Any initial change of color, which may develop when the test panel is heated during soldering, is disregarded; subsequent development of green-blue discoloration with observation of pitting of the copper panel or excrescences at the interfaces of the flux residue and copper boundary is regarded as major corrosion.

The results are summarized in the Table 8.

Table 8. Copper mirror and corrosion test results

Paste	Nature	Flux type according to specification	Picture of copper mirror	Copper mirror test result	Corrosion test result	Picture of corrosion test
A	WS	ORH0		H	Major	
B	WS	ORH1		H	Major	
C	WS	ORH1		H	Major	
D	NC	ROL0		L	No	
E	NC	ROL0		L	No	
F	NC	ROL1		L	Minor	

Surface Insulation Resistance (SIR)

Water-soluble solder pastes are designed to be cleaned after soldering: SIR values given in the datasheet of cleanable solder pastes are measured after complete removal of their residues. However, in order to observe the effect of non-cleaned or poorly cleaned corrosive residues, it was decided to measure the surface insulation resistance of all the pastes according to IPC-TM 650 method 2.6.3.3 without prior cleaning. The solder pastes were printed onto IPC B24 coupons (track/space width 0.4/0.5mm) and the coupons were reflowed using P1 thermal profile. Additional coupons for pastes A and D were made and cleaned before SIR as references. Boards were placed in the chamber and the test took place at 85°C and 85% relative humidity for 168 hours. A graph is presented in Figure 8: values of water-soluble solder pastes without cleaning all drop under the limit within the first 24 hours; A and C remain under the limit till the end of the test while B recovers. Pastes D, E, F as well as pastes A and D after residue removal all meet the requirements. Dendrite growth was observed for pastes A, B and C (pictures of C and D are presented in Figure 9).

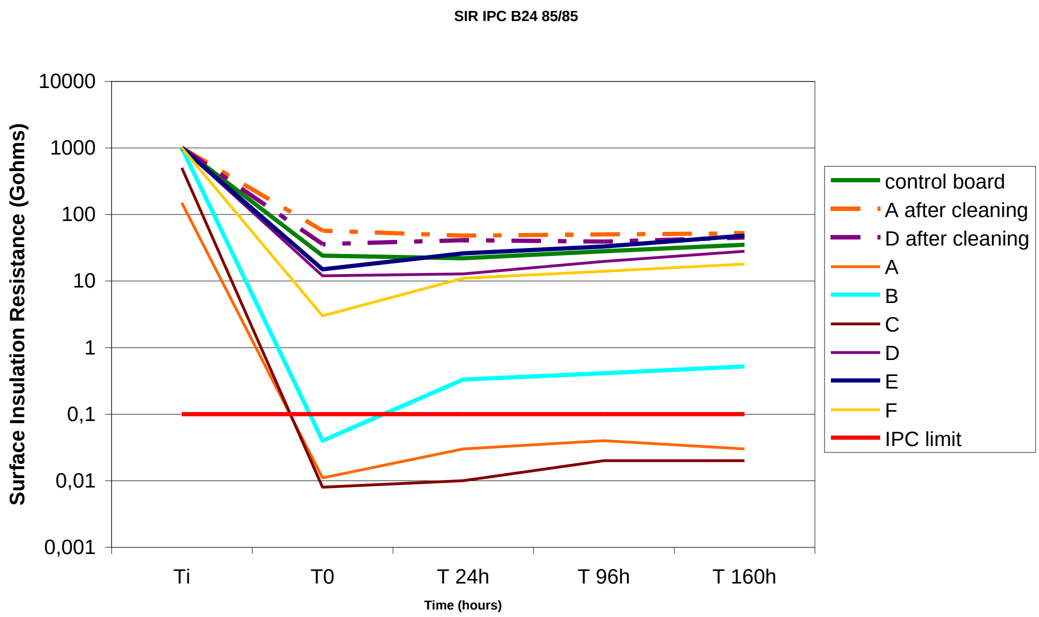


Figure 8. Surface Insulation Resistance graph

Figure 9. Observation under back-light a) Dendrites with paste C, b) No dendrite with paste D

<u>Cleanability</u>

Water-soluble solder pastes are designed to be cleaned using hot water only as they already contain saponifiers and/or surfactants allowing their removal. On the other hand, no-clean solder pastes cannot be cleaned using hot water only. Nevertheless it was decided to submit all the pastes to the same cleaning tests. The wetting test boards with OSP finish were used: one CSP 84 3 rows 0.5mm pitch 7mm² and several 0603 chips were placed (see Figure 6). After reflow with P5 thermal profile, the boards were cleaned in a water-based spraying machine. Five conditions were used: cold deionized (DI) water, 50°C DI water, 65°C DI water, 50°C DI water with 5% detergent, 50°C DI water with 25% detergent; each cleaning cycle was set to 10 minutes and was followed by a rinsing step with DI water and a drying step of 5 minutes at 80°C with hot air. The cleanliness was evaluated by visual inspection under binocular. The boards were considered clean when no residues were detected. Results are summarized in the table below (Table 9). An ionic contamination test was performed on the boards regardless of their cleanliness level. This test was done in accordance with the IPC-TM-650, method 2.3.25C: the board is immersed in a solution of water/isopropanol while analyzing the evolution of this cleaning solution contamination which circulates in closed-circuit inside the contaminometer. The results are expressed in µg equivalent NaCl per cm² of circuit and are reported in Table 9. A test board with no paste but submitted to the same reflow profile was used as control board: its ionic contamination measured was 0.21µg/cm².

Table 9. Cleanliness according to cleaning method (Visual / Ionic contamination)

Paste	A	B	C	D	E	F
Water cold	OK	NOK	NOK	NOK	NOK	NOK
	0.46	2.04	>3	0.29	0.28	0.30
Water 50°C	OK	NOK	OK	NOK	NOK	NOK
	0.18	1.57	0.20	0.45	0.37	0.44
Water 65°C	OK	OK	OK	NOK	NOK	NOK
	0.25	0.14	0.14	0.56	0.42	0.57
Water 50°C / detergent D 5%	OK	OK	OK	NOK	NOK	NOK
	0.22	0.19	0.21	0.40	0.43	0.84
Water 50°C / detergent D 25%	OK	OK	OK	OK	NOK	OK
	0.18	0.20	0.18	0.23	0.34	0.16

Paste A was the easiest to clean, even using cold water, followed by paste C and B for WS solder pastes. Cleanability of pastes D and F was achieved using detergent at 25% whereas E was not (a second cycle in the same conditions was necessary to clean it properly). As long as the cleaning was successful, the ionic contamination levels were acceptable and far below the MIL and DEF criteria (respectively 1.3µg/cm² and 1.5µg/cm²) for all the pastes. But, in case of incomplete cleaning, the level of ionic contamination for WS solder pastes was above specifications. On the contrary, all no-clean solder pastes showed an ionic contamination level below the specifications. Some pictures of the boards are given as examples of poor and good cleaning in Figure 10 and 11.

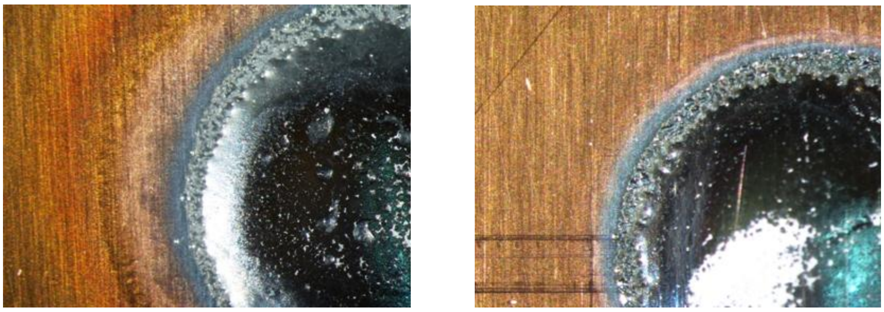


Figure 10. Poor / good cleaning on wetting H pattern

a) Paste B / poor **b) Paste B / good**

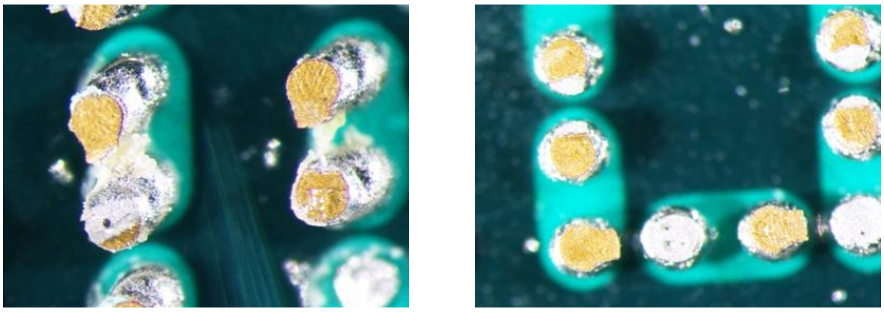


Figure 11. Poor / good cleaning under CSP (after removal)
a) Paste B / poor b) Paste B / good

Discussion

Wettability on copper coupons was generally worse for water-soluble pastes using long preheat on hotplate and in reflow oven. Nevertheless opposite results were obtained when using FR4 substrates with cleaned copper finish: larger wetting diameters were found for WS pastes and a slight dewetting for no-clean paste D was observed. These results were confirmed using the wetting test board with OSP finish. On the other hand, the same wetting test board with ENIG finish has led to more mixed results: wetting performance was dependant on solder pastes and on pattern types. Pastes A, E and F gave similar results, C and B were behind; the only constant was the poor performance of paste D for all patterns and graping on small deposits. WS solder pastes have demonstrated more predispositions to generate tombstoning than no-clean solder pastes. In terms of residue corrosiveness, due to their formulation, WS pastes exhibited high corrosivity as far as copper mirror, corrosion on copper and surface insulation resistance tests are concerned. And, due to their chemistry, their residues were also easily cleaned with water only, paste A being the best, then C and B. However, in case of incomplete cleaning, the ionic contamination was very high for water-soluble solder paste while it remained low for incomplete cleaning of no-clean solder pastes.

Conclusion

The purpose of the paper was to highlight the differences between water-soluble and no-clean solder pastes in order to guide users in their choice. To achieve this goal, six lead-free solder pastes were extensively studied, three being water-soluble and three being no-clean. In the first part of the paper, water-soluble pastes generally yielded results below the no-clean pastes with a significant sensitivity to temperature and humidity, a tendency to slump during preheat and a narrower printing window. It was concluded that the WS pastes had to be stored, handled and used with more caution before reflow compared to no-clean pastes. In the second part of the paper, regarding wetting properties, WS pastes rank generally better, especially for oxidized substrates. As far as cleanability is concerned, of course only water-soluble pastes can be cleaned with water only whereas no-clean pastes need detergent to achieve a complete removal of their residues. However, in case of poor cleaning, as the amount of ionic species usually found in WS residues is high (presence of ionic surfactants especially), the risk of corrosion is very high: this is the major drawback of such pastes.
The use of water-soluble pastes generally takes place in high reliability assembly as Medical, Military or Aerospace fields where close attention is paid to the quality of substrates, components, where reflow is done in inert atmosphere (nitrogen, vapor phase or under vacuum ovens) and where cleaning is compulsory for the majority of the products. The use of aggressive chemistry may not be necessary when using such equipments. Moreover, the risk of tombstoning is increased. In such fields, in case of new solder paste evaluation, it is useful to also consider the option of no-clean solder pastes in comparison with water-soluble solder pastes and even to think about review the whole cleaning process. This paper can then be used as a guide to study the critical aspects of these two types of solder pastes.

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References

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